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# ANISOTROPIC LIGHT SCATTERING BY SOLUTIONS OF LARGE MACROMOLECULES ORIENTED IN THE INTENSE ELECTRIC FIELDS OF LASER BEAMS

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## SYNOPSIS

Light scattering by monodisperse solutions of rigid anisotropic rod-like macromolecules of length  $l$ , of the same order as the wavelength  $\lambda$ , reoriented in the strong electric field of linearly polarized laser light is discussed. This discussion is based on numerical calculations of the relative variations in intensity  $\delta H_v^{h,v}$ ,  $\delta H_h^{h,v}$ ,  $\delta V_h^{h,v}$ ,  $\delta V_v^{h,v}$  of the light scattering components, induced by a laser beam of high intensity  $I_L^{h,v}$  polarized horizontally or vertically to the plane of observation. Calculations are made for various values of  $q_L^{h,v}(\omega_L) = [(a_3^{\omega_L} - a_1^{\omega_L})I_L^{h,v}/2kT]$  (the reorientation parameter of the optical polarizability ellipsoid with principal polarizabilities  $a_3^{\omega_L}$ ,  $a_1^{\omega_L}$  for the laser frequency  $\omega_L$ ) and for the three values  $l/\lambda = 0.5, 1, \text{ and } 2$ .

## INTRODUCTION

The light scattered by a monodisperse solution of rigid macromolecules, aligned into the direction of an external electric, magnetic, or optical field, provides a clue to their electric, magnetic, and geometrical properties [1-3].

The earliest theoretical studies of this kind are due to Wippler and Benoit [4], who considered the effect of a weak static electric field on light scattering by solutions of large macromolecules, representing a particular case of the Rayleigh-Debye-Gans approximation [5, 6]. Stoylov [7, 8] extended these considerations to strong electric fields including saturation.

Ravey [9] gave a description of light scattering for arbitrarily oriented macromolecules in the shape of spheres, disks, rods, and Gaussian chains, placed in a static electric field acting along the external bisectrix of the angle of observation.

Kielich [10, 11] proposed a theory of nonlinear light scattering by solutions of small macromolecules with linear dimensions  $l$  much smaller than the light wavelength  $\lambda$ , taking into account their complete alignment in a static electric and magnetic field as well as in the field of laser light. He also proposed a method for the determination of the optical anisotropy of such macromolecules. The problem has been discussed recently for small spheroids by Farinato [12].

Here, we shall extend the theory [10, 11] based on the relative intensity variations  $\delta V_v^{h,v}$ ,  $\delta H_h^{h,v}$ ,  $\delta V_h^{h,v}$ ,  $\delta V_v^{h,v}$  of the scattered light components to the case of solutions of large, rod-like macromolecules with linear dimensions  $l$  of the

order of  $\lambda$ , reoriented by the strong electric field of laser light polarized horizontally, or vertically, to the plane of observation. Our numerical calculations of the relative variations in intensity are carried out for three values of  $l/\lambda$ , namely, 0.5, 1, and 2, and for certain values of the reorientation parameter of the ellipsoid of optical polarizabilities. We have performed a similar analysis [13] for large rod-like macromolecules, oriented in a static electric field applied perpendicularly to the plane of observation.

### THEORY

We consider monodisperse dilute solutions of large, rigid, anisotropic macromolecules, not absorbing energy, and having the shape of a rod with rotational ellipsoid symmetry. We assume the symmetry axis of their optical properties to coincide with their geometrical axis.

The optical anisotropy of such macromolecules is given by Langevin's formula

$$\kappa_{\omega} = \frac{a_3^{\omega} - a_1^{\omega}}{a_3^{\omega} + 2a_1^{\omega}} \quad (1)$$

where  $a_3^{\omega}$  and  $a_1^{\omega}$  denote, respectively, the optical polarizability of the macromolecule in the direction of its symmetry axis (principal 3-axis) and perpendicular to it;  $\omega$  is the frequency of the incident probe light wave.

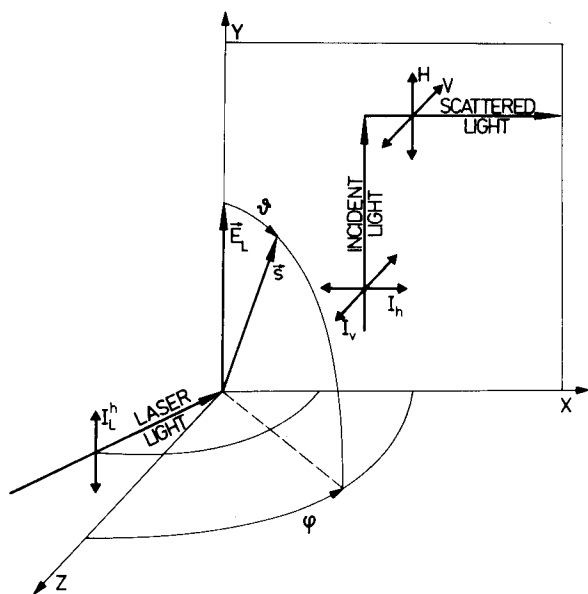


FIG. 1. The probe light beam of frequency  $\omega$  is incident along  $Y$  with indices  $v$  and  $h$  denoting, respectively, vertical and horizontal polarization. Scattered light observation is performed along  $X$ , with  $V$  and  $H$  standing for the vertical and horizontal component of scattered light.  $\vartheta$  is the angle between  $Y$  and the symmetry axis  $\vec{s}$  of the macromolecule.  $\varphi$  is the azimuth of  $\vec{s}$ . The strong laser beam (intensity  $I_L^h$ , frequency  $\omega_L$ ), the electric field  $\vec{E}_L$  of which reorients the macromolecules, is polarized horizontally along  $Y$  and propagates in the  $XZ$ -plane.

We assume that the weak probe light beam is incident along the laboratory  $Y$ -axis, and that observation takes place in the direction of the  $X$ -axis. Figure 1 visualizes the various possible polarization directions of the incident and scattered waves. Assume the system to be acted on simultaneously by the electric field of a strong laser beam of intensity  $I_L^{\text{v,h}}$  polarized vertically (superscript v), or horizontally (h), to the plane of observation.

The laser beam-induced relative variations in vertical and horizontal light scattering components, at vertical and horizontal polarization of the probe beam (subscripts v, h), are in general given by [3]

$$\delta V_{\text{v}}^{\text{v,h}} = \frac{1}{V_{\text{v}}^0} \langle \{1 + 2\kappa_{\omega}(3c_{z3}^2 - 1) + \kappa_{\omega}^2(9c_{z3}^2 - 6c_{z3}^2 + 1)\} R^2(c_{b3}) \rangle_{I_L^{\text{v,h}}} - 1 \quad (2)$$

$$\delta V_{\text{h}}^{\text{v,h}} = \frac{1}{V_{\text{h}}^0} \langle c_{x3}^2 c_{z3}^2 R^2(c_{b3}) \rangle_{I_L^{\text{v,h}}} - 1 \quad (3)$$

$$\delta H_{\text{v}}^{\text{v,h}} = \frac{1}{H_{\text{v}}^0} \langle c_{y3}^2 c_{z3}^2 R^2(c_{b3}) \rangle_{I_L^{\text{v,h}}} - 1 \quad (4)$$

$$\delta H_{\text{h}}^{\text{v,h}} = \frac{1}{H_{\text{h}}^0} \langle c_{x3}^2 c_{y3}^2 R^2(c_{b3}) \rangle_{I_L^{\text{v,h}}} - 1 \quad (5)$$

$c_{x3}$ ,  $c_{y3}$ ,  $c_{z3}$ , and  $c_{b3}$  are cosines of the angles between the laboratory axes  $X$ ,  $Y$ ,  $Z$ , and the external bisectrix  $b$  of the observation angle  $\Theta$  and the symmetry axis  $\bar{s}$  (3-axis) of the macromolecule.

In eqs. (2)–(5), we have introduced the following reduced intensity components of light scattered in the absence of a strong laser beam [5]:

$$\begin{aligned} V_{\text{v}}^0 &= (1 - \kappa_{\omega})^2 \left[ \frac{Si(2K)}{K} - \left( \frac{\sin K}{K} \right)^2 \right] \\ &+ 3\kappa_{\omega}(1 - \kappa_{\omega}) \left[ \frac{Si(2K)}{K} + \frac{\sin 2K}{4K^3} - \frac{1}{K^2} + \frac{\cos 2K}{2K^2} \right] \\ &+ \frac{27}{8} \kappa_{\omega}^2 \left[ \frac{Si(2K)}{K} - \frac{4}{3K^2} - \frac{\cos 2K}{4K^4} + \frac{\sin 2K}{4K^3} + \frac{\cos 2K}{2K^2} + \frac{\sin 2K}{8K^5} \right] \end{aligned} \quad (6)$$

$$V_{\text{h}}^0 = H_{\text{v}}^0 = \frac{Si(2K)}{16K} + \frac{\cos 2K}{32K^2} + \frac{\sin 2K}{64K^3} + \frac{3 \cos 2K}{64K^4} - \frac{3 \sin 2K}{128K^5} \quad (7)$$

$$H_{\text{h}}^0 = \frac{3Si(2K)}{32K} - \frac{1}{6K^2} + \frac{3 \cos 2K}{64K^2} - \frac{5 \sin 2K}{128K^3} - \frac{19 \cos 2K}{128K^4} + \frac{19 \sin 2K}{256K^5} \quad (8)$$

The symbol

$$\langle (\dots) \rangle_{I_L^{\text{v,h}}} = \int_0^{2\pi} \int_0^{\pi} (\dots) f(\vartheta, I_L^{\text{v,h}}) \sin \vartheta d\vartheta d\varphi \quad (9a)$$

stands for averaging over all orientations of the macromolecules in the electric field of the strong laser beam  $I_L^{\text{v,h}}$  (polarization v or h) with distribution function in the form:

$$f(\vartheta, I_L^{\text{v,h}}) = \frac{\exp(q_L^{\text{v,h}} \cos^2 \vartheta)}{\int_0^{2\pi} \int_0^{\pi} \exp(q_L^{\text{v,h}} \cos^2 \vartheta) \sin \vartheta d\vartheta d\varphi} \quad (9b)$$

where  $\vartheta$  is the angle between the direction of the strong electric field of the laser beam and the symmetry axis  $\vec{s}$ , and [10]

$$q_L^{v,h}(\omega_L) = \frac{(a_3^{\omega_L} - a_1^{\omega_L})}{2kT} I_L^{v,h} \quad (10)$$

is the dimensionless reorientation parameter of the ellipsoid of optical polarizabilities at the laser frequency  $\omega_L$ . In addition,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. In the Rayleigh-Debye-Gans approximation, the function  $R(c_{b3})$  for rod-like macromolecules is of the form [6]:

$$R(c_{b3}) = \frac{\sin(Kc_{b3})}{Kc_{b3}}, \quad (11)$$

where  $K = \{[2\pi l \sin(\Theta/2)]/\lambda\}$  is a parameter which depends on the length  $l$  of the macromolecule, the angle of observation  $\Theta$ , and the probe beam wavelength  $\lambda$ .

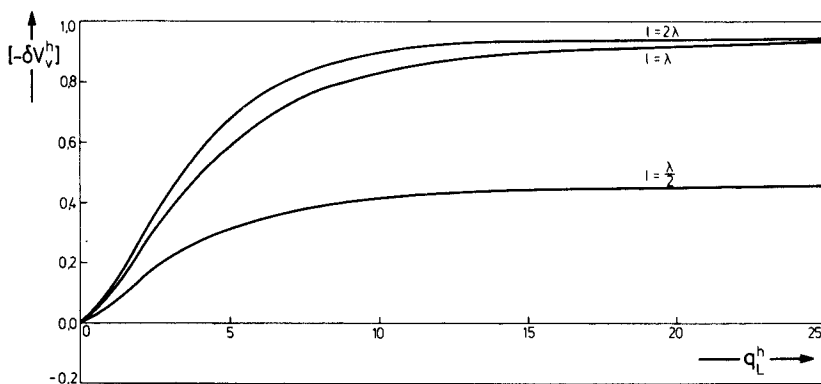


FIG. 2. The relative variation  $[-\delta V_v^h]$  as a function of the reorientation parameter  $q_L^h$  at  $\kappa_\omega = 0.1$ .

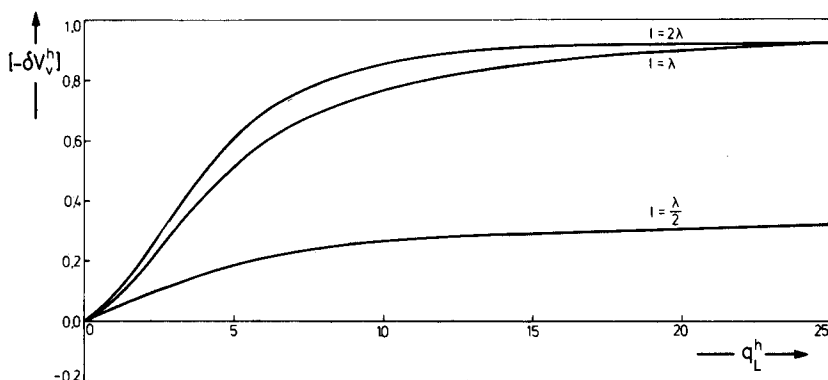


FIG. 3. The relative variation  $[-\delta V_v^h]$  vs. the reorientation parameter  $q_L^h$  at  $\kappa_\omega = 0$ .

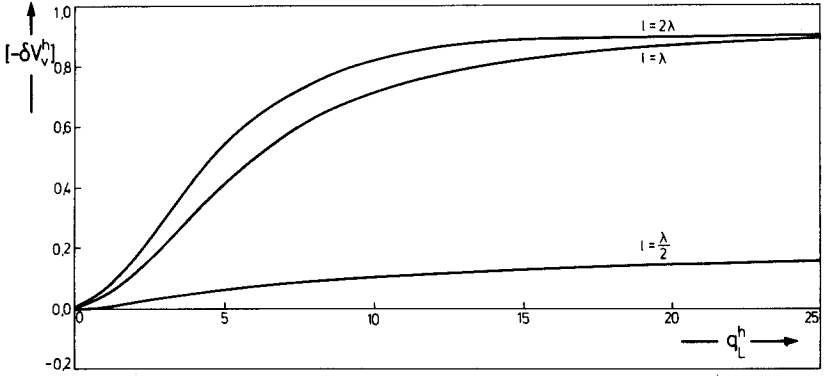


FIG. 4. The relative variation  $[-\delta V_v^h]$  vs. the reorientation parameter  $q_L^h$  at  $\kappa_\omega = -0.1$ .

### Case a

The inducing laser beam is polarized vertically.

The relative variations [2-5] of the components of light, scattered due to the laser beam being polarized vertically, are expressed similarly to those due to a static electric field, acting perpendicularly to the plane of observation [13]. In order to obtain the expressions of ref. [13], one has to perform in eqs. (2)-(5) the following substitutions:

$$c_{x3} = \sin \vartheta \cos \varphi$$

$$c_{y3} = \sin \vartheta \sin \varphi$$

$$c_{z3} = \cos \vartheta$$

$$c_{b3} = \sin \vartheta \cos \left( \varphi + \frac{\pi}{4} \right)$$

where  $\varphi$  is the azimuth of the symmetry axis  $\vec{s}$ .

### Case b

The inducing laser beam is polarized horizontally.

The relative variations [2-5] of the components, scattered due to the laser beam polarized horizontally (i.e., when the direction of linear polarization of the laser beam coincides with the  $Y$ -axis and the laser beam propagates in the  $XZ$ -plane, Fig. 1) are obtained with the directional cosines  $c_{x3} = \sin \vartheta \cos \varphi$ ,  $c_{y3} = \cos \vartheta$ ,  $c_{z3} = \sin \vartheta \sin \varphi$ , and  $c_{b3} = (-\sin \vartheta \cos \varphi + \cos \vartheta)/\sqrt{2}$ , as follows:

$$\begin{aligned} \delta V_v^h = \frac{1}{V_v^0} \{ & 2[1 + 2\kappa_\omega(3 \sin^2 \vartheta \sin^2 \varphi - 1) + \kappa_\omega^2(9 \sin^4 \vartheta \sin^4 \varphi \\ & - 6 \sin^2 \vartheta \sin^2 \varphi + 1)] \sin^2 [K(-\sin \vartheta \cos \varphi \\ & + \cos \vartheta)/\sqrt{2}]/K^2(-\sin \vartheta \cos \varphi + \cos \vartheta)^2 \} I_E^h - 1 \end{aligned} \quad (12)$$

$$\delta V_h^h = \frac{1}{V_h^0} \{ 2 \sin^4 \vartheta \cos^2 \varphi \sin^2 \varphi \sin^2 [K(-\sin \vartheta \cos \varphi$$

$$+ \cos \vartheta) / \sqrt{2}] / K^2 (-\sin \vartheta \cos \varphi + \cos \vartheta)^2)_{I_E} - 1 \quad (13)$$

$$\delta H_v^h = \frac{1}{H_v^0} \{ 2 \cos^2 \vartheta \sin^2 \vartheta \sin^2 \varphi \sin^2 [K] - \sin \vartheta \cos \varphi + \cos \vartheta / \sqrt{2} \} / K^2 (-\sin \vartheta \cos \varphi + \cos \vartheta)^2)_{I_E} - 1 \quad (14)$$

$$\delta H_h^h = \frac{1}{H_h^0} \{ 2 \sin^2 \vartheta \cos^2 \vartheta \cos^2 \varphi \sin^2 [K] (-\sin \vartheta \cos \varphi + \cos \vartheta) / \sqrt{2} \} / K^2 (-\sin \vartheta \cos \varphi + \cos \vartheta)^2)_{I_E} - 1 \quad (15)$$

In this case, the relative variations of the cross-components  $H_v$  and  $V_h$  are not equal to each other, i.e., they behave contrary to the case of vertical polarization of the laser beam (when, as we remember,  $\delta H_v^v = \delta V_h^v$  at  $\vartheta = 90^\circ$ ).

The following relations hold between the relative variations due to a laser beam horizontally polarized along the  $Y$ -axis (Eqs. (12)–(15)) and those caused by a laser beam polarized along the  $X$ -axis:

$$\delta V_v^Y = \delta V_v^X$$

$$\delta V_h^Y = \delta H_h^X$$

$$\delta H_v^Y = \delta V_h^X$$

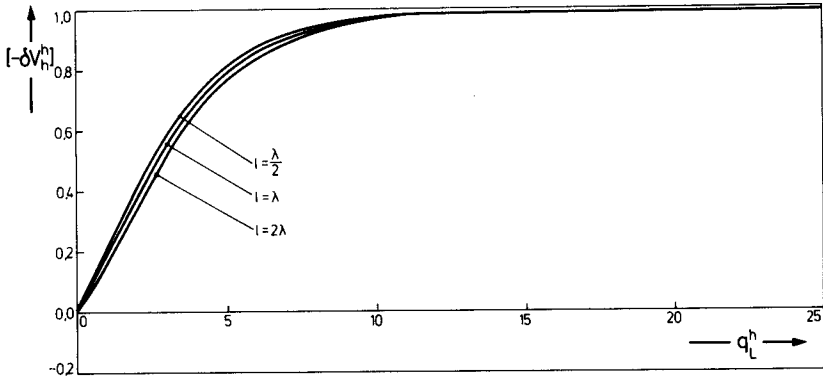


FIG. 5. The relative variation  $[-\delta V_h^h]$  vs. the reorientation parameter  $q_L^h$ .

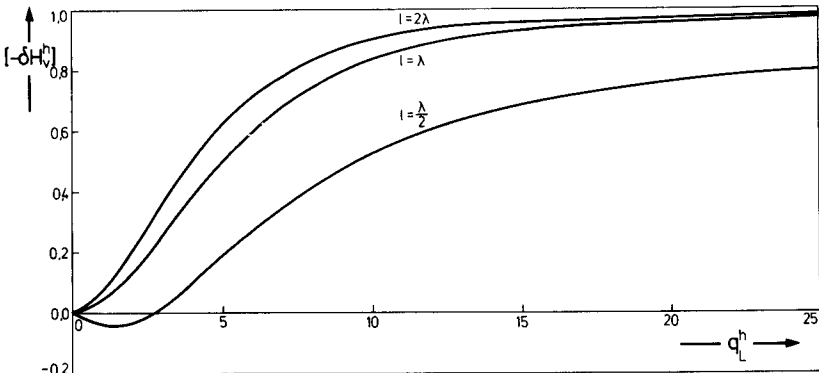


FIG. 6. The relative variation  $[-\delta H_h^h]$  as a function of the reorientation parameter  $q_L^h$ .

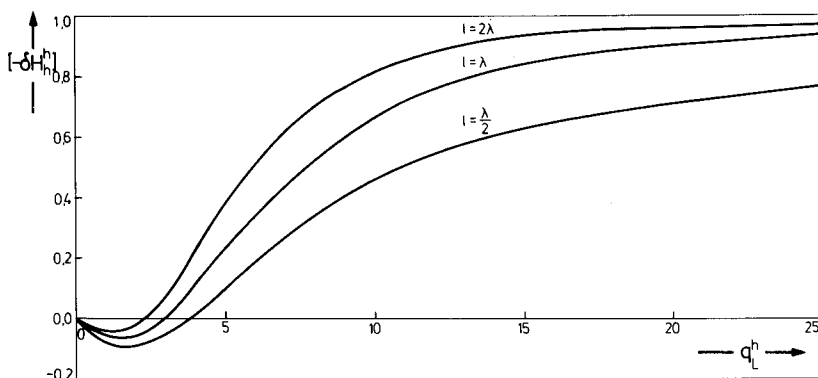


FIG. 7. The relative variation  $[-\delta H_h^h]$  as a function of the reorientation parameter  $q_L^h$ .

$$\delta H_h^Y = \delta H_h^X \quad (16)$$

## DISCUSSION

The various relative changes in intensity of the scattered light components given by eqs. (2)–(5) for small macromolecules are expressed in terms of generalized Langevin functions [11] of the variable  $q_L^h$ . For large macromolecules, we calculated numerically the intensity components in the form of eqs. (12)–(15) as functions of the parameter  $q_L^h$  for three values of  $l/\lambda$ : 0.5, 1, and 2 (Figs. 2–7).

Since the curves of  $\delta V_v^v$ ,  $\delta V_h^v$ ,  $\delta H_v^v$ , and  $\delta H_h^v$  versus the parameter  $q_L^v$  are identical with those studied in [13] for nondipolar macromolecules oriented in a static electric field, we refrain from considering them here.

It is known from [10] and [11] that, between the relative changes in intensity components of light scattered by small macromolecules in the presence of a vertically polarized laser beam and the respective relative variations in the presence of a laser beam polarized horizontally (in the direction of the  $Y$ -axis), the following well defined analytical relations hold:  $\delta H_h^v = \delta V_h^h$ ,  $\delta H_v^v = \delta V_h^v = \delta H_v^h = \delta H_h^h$ .

These relations no longer hold numerically for large macromolecules. Nonetheless, the functions [13]  $\delta H_h^v = f(q_L^v)$  and  $\delta V_h^v = f(q_L^h)$  (Fig. 5) and  $\delta H_v^v = \delta V_h^v = f(q_L^v)$  and  $\delta H_v^h, \delta H_h^h$  plotted versus the parameter  $q_L^h$  (Figs. 6 and 7) are similar in shape, respectively.

The relative variations  $\delta H_v^h$  and  $\delta H_h^h$  at horizontal laser beam polarization in the  $Y$ -direction (Figs. 6 and 7) are positive only in a narrow range of positive  $q_L^h$  values. For all other  $q_L^h > 0$ , they are negative. The variations and  $\delta V_h^h$  (Figs. 5 and 2–4) are negative for all  $q_L^h > 0$  because of an additional weakening in intensity of the components of light, scattered due to the orienting electric field of the horizontally polarized laser beam.

The relative variations  $\delta V_v^h, \delta H_v^h, \delta V_h^h$ , and  $\delta H_h^h$  depend strongly on  $L/\lambda$  (in this work,  $l/\lambda = 0.5, 1, 2$ ). The curve showing this dependence is different for  $\delta V_h^h$  (Fig. 5) than in the case of  $\delta V_v^h, \delta H_v^h$ , and  $\delta H_h^h$  (Figs. 2–4, 6, and 7). Thus,

for fixed  $q_L^h$ , the values of  $\delta V_h^h$  increase with increasing  $l/\lambda$ , whereas  $\delta V_v^h$ ,  $\delta H_v^h$ , and  $\delta H_h^h$  decrease. The increase in  $\delta V_h^h$  can be explained as being due to the considerable weakening of the component  $\delta V_h^h$  by the orienting field and by the fact that the differences in  $V_h^h$  for different  $l/\lambda$  are much less than the differences in  $V_h^0$ , so that  $\delta V_h^h$  is more essentially affected by the component  $V_h^0$  (which decreases as  $l/\lambda$  increases). The differences in  $\delta V_h^h$  for different  $l/\lambda$  are small, and occur only in the initial range of  $q_L^h$  values. For other values of  $q_L^h$ , the value of  $\delta V_h^h$  becomes constant for all  $l/\lambda$ . The other components  $V_v^h$ ,  $H_h^h$ , and  $H_v^h$  are much less weakened, and the differences in these components for the different values of  $l/\lambda$  are significant; much greater than the differences in the case of  $V_v^0$ ,  $H_h^0$ , and  $H_v^0$ .

All the relative variations (Figs. 2-7) tend to a limiting value at given anisotropy ( $a_3^{\omega L} - a_1^{\omega L}$ ) and increasing laser beam intensity. The limiting value corresponds to optical saturation [10, 11]. Here, the relative variations  $\delta V_h^h$ ,  $\delta H_h^h$ , and  $\delta H_v^h$  attain a constant value, independent of the length of the macromolecules, i.e.,  $\delta V_h^h(q_L^h \rightarrow \infty) = \delta H_h^h(q_L^h \rightarrow \infty) = \delta H_v^h(q_L^h \rightarrow \infty) = -1$ . However, the limiting value to which  $\delta V_v^h$  tends depends on  $l/\lambda$  and the optical anisotropy  $\kappa_\omega$ , i.e.,  $\delta V_v^h(q_L^h \rightarrow \infty) = \{[2(1 - \kappa_\omega)^2 \sin^2(K/\sqrt{2})]/V_v^0 K^2\} - 1$ .

On comparing the relative variations at vertical [13] and horizontal polarization of the orienting laser beam, we note that the influence of macromolecular size is much greater (under the given experimental conditions) if the orienting beam is polarized horizontally.

A similar analysis can be carried out for the situation in which the experiment is conducted solely with a laser beam [10], of an intensity so high that its electric field suffices for inducing macromolecular reorientation, and thus is sufficient for the self-induction of nonlinear variations in the intensity components [eqs. (2)-(5)] of scattered light. Recently, the use of laser technique has made it feasible to observe induced optical birefringence due to reorientation of macromolecules in the electric field of a strong laser beam. Thus, an optical Kerr effect has been observed by Jennings and Coles [14] in solutions of polymers, by Coles and Jennings [15] and Dobek et al. [16] in solutions of biopolymers, and in the isotropic phase of nematic liquid crystals by Wong and Shen [17], Prost and Lalanne [18], Lalanne et al. [19], and Coles and Jennings [20]. These important observations of the new effect, rendering apparent the optical reorientation of macromolecules, point to the imminent possibility of actually performing observations of the laser light-induced changes in scattered light intensity discussed in this paper. The information on optical reorientation of macromolecules obtained by these methods can be compared with the data already available concerning electric reorientation of macromolecules in electro-optical phenomena [21, 22].

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